

Y3.N21/5:6/1882

NACA TN No. 1882

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

TECHNICAL NOTE

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OXIDATION CHARACTERISTICS OF MOLYBDENUM DISULFIDE AND
EFFECT OF SUCH OXIDATION ON ITS ROLE AS A
SOLID-FILM LUBRICANT

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Washington
May 1949

BUSINESS, SCIENCE
& TECHNOLOGY DEPT.

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SUMMARY

An experimental investigation was conducted to determine the oxidation characteristics of molybdenum disulfide MoS_2 and to determine the effect of such oxidation on its role as a solid-film lubricant. The rate of the oxidation of molybdenum disulfide was investigated using X-ray diffraction techniques in which specimens could be heated in vacuum as well as in air. Phase changes occurring to molybdenum disulfide while being heated to various temperatures in vacuum were also investigated by X-ray diffraction. The change in the coefficient of friction with sliding velocity was determined for surfaces coated with molybdenum disulfide in various degrees of oxidation. The friction experiments were conducted with an apparatus that caused a spherical rider to slide in a spiral path on a rotating disk at a range of velocities between 50 and 8000 feet per minute and a load of 269 grams (126,000 lb/sq in., initial Hertz surface stress).

A coating of molybdenum disulfide serving as a high-temperature solid-film lubricant maintained low coefficient-of-friction values during its oxidation as long as an effective subfilm of the molybdenum disulfide remained. Films of the oxidation product of molybdenum disulfide, namely molybdenum trioxide, alone produced very high friction. Molybdenum disulfide began to oxidize at a very low rate when heated in air at 750°F , the rate increasing steadily and becoming high at 1050°F and above. Molybdenum disulfide maintained its original hexagonal structure when heated to 1000°F in vacuum.

INTRODUCTION

The characteristics of molybdenum disulfide MoS_2 indicate that it may be suitable for lubricating sliding surfaces, the

temperature of which is too high for ordinary lubricants, or where circumstances are such that an ordinary lubricant cannot be used as, for example, with fluids or organic vapors prohibited, with high centrifugal forces present, or in vacuum or low pressure applications. Molybdenum disulfide is favorably considered as a special lubricant because of the following properties: (1) laminated structure with crystals exhibiting excellent basal cleavage, (2) relative lack of brittleness, and (3) relative chemical stability. Reference 1 describes the use of MoS_2 as a high-temperature lubricant in applications where temperatures reach several hundred degrees, and states that MoS_2 is resistant to oxidation at these temperatures. This compound is discussed as a special lubricant for the bearing of a rotating X-ray tube in reference 2 and as a die lubricant in reference 3. These are applications in which an ordinary lubricant could not be used. In reference 4, it is shown that MoS_2 was very effective as a solid-film lubricant particularly at high sliding velocities and reference 5 shows that it is effective at high pressures.

An investigation was conducted at the NACA Lewis laboratory to determine: (1) the change in the crystalline structure of MoS_2 heated in the absence of oxygen; (2) the oxidation characteristics of MoS_2 ; and (3) the effect of such oxidation on its role as a solid-film lubricant.

A coating of MoS_2 that serves to lubricate two sliding surfaces can be subjected to extremes of temperature and pressure and to a wide variation in the concentration of other materials with which it might react. Under conditions of high temperatures, low pressures, and low concentrations of reacting materials, MoS_2 could experience a phase change without a chemical reaction. The hexagonal structure, with a high ratio of height to breadth of unit cell c/a of 12.30 (reference 6), is partly credited with giving MoS_2 its desirable lubricating properties. It is therefore desirable to determine the phase change, if any, that occurs to MoS_2 when heated from room temperature to 1200°F in vacuum.

The nature of the oxidation of MoS_2 is of primary importance in considering it as a high-temperature lubricant. Under most lubricating applications, oxygen will be present and oxidation will occur to a degree dependent upon several factors, the more important probably being the concentration of oxygen and the temperature. The MoS_2 is roasted as an ore at 1200°F and a preliminary investigation revealed that a coating of MoS_2 applied as in reference 4 will readily and completely oxidize at the same temperature. At a

considerably lower temperature, MoS_2 begins to oxidize to molybdenum trioxide MoO_3 . Experiments were therefore performed utilizing X-ray diffraction techniques to determine the rate at which MoS_2 will oxidize from room temperature to 1100°F .

The effect on friction of partial and complete oxidation of a coating of MoS_2 serving as a lubricant between sliding surfaces was investigated by noting the change in the coefficient of kinetic friction of steel specimens coated with MoS_2 in various states of oxidation, including coatings completely oxidized to MoO_3 . The experiments were conducted at room temperature and the friction measurements were made using an elastically restrained spherical rider sliding in a spiral path on a rotating disk to give sliding speeds of 50 to 8000 feet per minute.

APPARATUS AND PROCEDURE

X-Ray Diffraction Technique

X-ray diffraction patterns obtained while the specimen was held at high temperatures required the use of the special equipment illustrated in figure 1. The specimen in the form of a cake was tied to the face of the resistance-type heater. The diffracted beam was detected by a scanning Geiger counter and recorded as a tracing. This method of obtaining the pattern causes loss of background detail and is limited to 45° of pickup but it does provide for high-temperature analysis.

The specimen was mounted under a housing to provide for the diffraction patterns taken at high temperature and low pressures (fig. 2). This apparatus is described in detail in reference 7. The chamber was evacuated to as low as 8×10^{-3} millimeters of mercury at the highest temperature of 1200°F . Celluloid windows permitted the entrance of the initial beam and the exit of the diffracted beam through the vacuum wall. The diffraction patterns from specimens at room temperature were obtained by mounting the sample on a thread and recording the diffracted beam on film with a Debye-Scherrer powder camera. Quantitative estimates were made by comparison of the unknown patterns with patterns of known composition. The minimum detectable amount by this X-ray method is commonly accepted as being 5 percent. A copper X-ray tube with a nickel filter was used.

Preparation of Specimens for X-Ray Diffraction

Molybdenum disulfide, commercially obtained, of a purity of 97 percent was used. For the high-temperature diffraction work, the MoS_2 was compressed into a cake in a mounting press and tied to the face of the heater. The temperature to which the specimen was heated was determined by embedding a chromel-alumel thermocouple within 2 millimeters of the surface of the cake. Because the X-ray diffraction pattern was obtained from surface material, the temperatures given are high. By touching a thermocouple to the surface and embedding one immediately below the surface, two values were obtained, which could be averaged to give an indication of the surface temperature. Variable surrounding conditions made use of this method impractical. Separate experiments indicated, however, that the surface temperature was approximately 50° less than the inner temperature at 800°F and 100° less at 1200°F .

The specimens for the powder camera were heated in an open crucible in an electric furnace and the temperature was determined by embedding a thermocouple in the material. Amounts used were such that the powder would not be over $1/16$ inch deep on the floor of the crucible. After cooling, a portion of the sample was mounted on a thread for the X-ray diffraction camera.

Friction Apparatus

The experimental friction studies were conducted with the equipment described in detail in reference 8. In figure 3, a diagrammatic sketch of the basic parts of the equipment, it can be noted that a loaded, spherical rider slides in a spiral path on a rotating disk. The friction force is measured by four strain gages mounted on a copper-beryllium dynamometer ring. The coefficient of friction is computed by dividing the measured friction force by the applied normal load. Sliding speeds from 50 to 8000 feet per minute and loads of 269 grams ($126,000\text{ lb/sq in.}$, initial Hertz surface stress) were employed.

Preparation of Specimens for Friction Experiments

A disk coated with MoS_2 in a manner described in reference 4 (where MoS_2 was mixed with an organic binder, commercial corn syrup, into a thick paste and painted on the disk heated to 650°F) was used in making the partly oxidized specimens. The MoS_2 coating

was not rerun but the data from reference 4 are included and used as a reference. In addition, the data from the clean disk of reference 8 are included for comparative purposes.

Whenever the surface was treated to determine effect on friction, only the disk specimens were so treated. In order to obtain partial oxidation of the MoS_2 coating, the disk was placed in a muffle furnace and heated for 1/2 hour at 1000°F . This treatment produced a top layer primarily of MoO_3 over an unoxidized portion immediately adjacent to the steel, which is representative of the coating on which the rider is sliding. A photograph of a small specimen treated in this manner is presented in figure 4. Three zones have been exposed by abrasion and identified by electron diffraction, namely: the yellowish-white area of MoO_3 , the mixed layer of MoS_2 , carbon, and iron oxides, and the bare steel.

A film of MoO_3 , the completely oxidized product of the MoS_2 , was made by painting the clean hot disk with syrup only and then evaporating MoO_3 on the surface with the equipment shown in figure 5. Molybdic acid H_2MoO_4 was placed in the crucible and heated with the forced draft Meker burner. The acid dehydrated and became MoO_3 , which melted, evaporated, and then condensed on the cool steel above. The disk was rotated at 10 rpm until a uniform film thickness of approximately 0.003 inch was deposited.

Steel disks without the initial syrup treatment but with a film of MoO_3 only were subjected to the friction experiments. In one case, coarse crystalline MoO_3 was rubbed on the plate. This rubbing essentially resulted in filling the microscopic valleys of the steel surface. In a second case, the material was evaporated; in both cases the MoO_3 was deposited on a clean disk that lacked the pretreatment.

RESULTS AND DISCUSSION

MoS_2 Heated in Presence of Oxygen

When MoS_2 is heated in air at atmospheric pressure, it oxidizes at a rate depending primarily on the temperature. The amount of the oxidation product depends on the time of exposure. When a small amount of MoS_2 is heated in an open crucible, the degree of oxidation can be qualitatively determined simply by noting the color change. No color change occurred for 5 hours at 800°F but, from that time on, oxidation was in evidence and the whole amount had been converted from gray-black to yellowish-white at the

end of 17 hours. At 900° F, only 1/2 hour was required and, at 1000° F, oxidation was complete in a few minutes. X-ray diffraction patterns were obtained from crucible samples heated to various temperatures (800°, 850°, 900°, and 1000° F) for 1/2 hour. Figure 6 presents reproductions of the original diffraction patterns of these crucible samples after 1/2 hour of heating. The patterns are aligned to reveal the status of the conversion of MoS₂ to MoO₃. The most intense and identifying lines of MoS₂ can be seen to decrease in intensity with increasing temperature and to disappear almost completely when MoS₂ is heated for 1/2 hour at 1000° F. The pattern of MoO₃ gradually appears and becomes predominant.

From these data, the ratio of the amount of the hexagonal crystals to the amount of orthorhombic crystals in the mixture has been approximated:

Temperature, (°F)	Ratio of hexagonal to orthorhombic crystals
800	20
850	10
900	1
1000	.05

The time required to oxidize the coating of MoS₂ at the various temperatures was also determined. Figure 7 is a reproduction of a sample of the original tracings of the diffraction patterns obtained by the second method wherein the pattern was recorded with the specimen of MoS₂ at the high temperatures. The figure shows that the pattern of MoO₃ becomes increasingly dominant as the temperature increases from 800° to 1000° F.

A plot of the data obtained with the high-temperature X-ray diffraction camera showing the change with time, of the ratio A/B, which is a measure of the degree of oxidation of MoS₂ to MoO₃, is shown in figure 8. In the ratio, A is the height of the curve of the most intense diffraction line of MoO₃ during partial oxidation and B is the height of the curve of the most intense diffraction line of MoO₃ at complete oxidation.

At a given temperature, the height of the curves for any component of a mixture will vary with the composition of the mixture. This variation in height was considered as an indication of the change in percentage of MoO₃ in a mixture of MoS₂ and MoO₃. Theoretically, the area under a given curve in tracings for a specimen of fixed composition remains constant with change in

temperature. This relation was confirmed by noting that the area did not vary more than 1 percent with great changes in height and width when the specimen was heated from room temperature to elevated temperatures. The data cover time intervals from 1 to 7 hours and temperatures from 900° to 1100° F. The slope of the curve increases with temperature, reaching complete oxidation in approximately 7 hours at 1100° F.

A summarization of results in respect to the nature of the oxidation of MoS_2 is presented in figure 9 in a form that can be used with ease in the interpretation of friction results. The figure shows the exponential nature of the oxidation relative to temperature for heating periods of 1/2 hour. Oxidation rates in various temperature ranges are shown. The rate of oxidation is expressed relative to the rate at 900° F, a temperature arbitrarily chosen for unit rate. Up to 750° F, no oxidation had been detected. Between 750° and 790° F, Ryozi (reference 9) found that an extremely thin film of MoO_3 was forming on a large single crystal of MoS_2 . The film could be detected only by electron diffraction. Between 790° and 850° F, the results reported herein have shown that slow but appreciable oxidation occurs, the oxide being of sufficient concentration to be detected by X-ray diffraction. Between 850° and 900° F, the oxidation becomes visible by virtue of the color change and, above 900° F, MoS_2 is oxidizing at an appreciable rate. If MoS_2 is serving as a lubricant for surfaces sliding at high temperatures, it can be expected that the MoS_2 will, if oxygen is present in sufficiently high concentrations, oxidize at a very low rate when heated in air at 750° F, the rate increasing steadily and becoming high at 1050° F and above.

Friction Characteristics

The manner in which the oxidation of a coating of MoS_2 will alter the friction characteristics has been determined. Disks coated with MoS_2 in various degrees of oxidation were subjected to friction experiments similar to those of reference 4. The finished coating of MoS_2 on the steel disk is composed of a mixture of carbon (from the syrup) and MoS_2 , which is bonded to the steel with an intermediate layer of several oxides of iron. In order to obtain partial oxidation, the disk was heated and conversion of MoS_2 began at the surface and proceeded inward to a degree depending on the time. An exposure of 1/2 hour at 1000° F oxidized approximately 75 percent of the MoS_2 and resulted in loss of the carbon as carbon dioxide CO_2 .

The friction data with MoS_2 in various degrees of oxidation are shown in figures 10 and 11. The data for MoS_2 from reference 4 is included for comparative purposes and this material is very effective as a solid-film lubricant at high sliding velocities. As seen in figure 10, the curve showing the friction characteristics of a disk treated with MoS_2 and then oxidized to form MoO_3 exhibits high friction at very low speeds, but above 1000 feet per minute, the coefficient of friction parallels very closely that of unoxidized MoS_2 . From these results, it can be presumed that in the case of partial oxidation of the MoS_2 coating, low friction is maintained because of the existence of underlying MoS_2 . That is, the underlying film of MoS_2 , which is adhering to the steel, is serving as the effective lubricating film and the coating of MoO_3 does not appreciably affect the friction characteristics. The conclusion can therefore be made that a coating of MoS_2 serving as a high-temperature solid-film lubricant will maintain low coefficient of friction during its oxidation as long as an effective subfilm of MoS_2 remains.

In order to determine the results with complete oxidation of MoS_2 in the coating, a disk was prepared by the same procedure except that only the organic binder was painted on the hot disk, the purpose being to simulate the underlying conditions without the presence of MoS_2 . A thin film of MoO_3 was then deposited on the disk by evaporation, as previously described. The results of the friction experiments on this disk are also shown in figure 10. The coefficient of friction of this evaporated film at the low speeds is in the same order as that for partly oxidized film. As the speeds increase, however, the friction coefficient remains appreciably higher than for either of the other two curves. This result indicates that when oxidation of MoS_2 is complete friction will increase to the values indicated.

The results obtained when the only film on the friction disk was MoO_3 are shown in figure 11. In the case where the material is simply rubbed on the steel, the coefficient of friction is extremely high at the low speeds and does not show a continuously decreasing trend with increase in velocity. The MoO_3 used in this experiment was coarse and examination revealed crystals to be simply lodged in the microscopic valleys of the surface with more than 50 percent of the bare metal exposed. It can be concluded that MoO_3 in this form is extremely detrimental and will increase friction. A change in the form of MoO_3 produced a change in the coefficient of friction, as can be seen in figure 11 for the evaporated MoO_3 curve. The friction coefficient is

extremely high at low velocities but shows a decreasing trend. The MoO_3 in this case was of very fine texture, like a powder. The MoO_3 by itself does not lubricate sliding steel surfaces, but adds to the friction produced by steel sliding on steel. This addition is evident by comparing the curves of the MoO_3 film with the curve of clean steel and noting that the MoO_3 film by itself generally produces higher coefficient of friction than the clean steel. The difference in the coefficient-of-friction values for the two evaporated MoO_3 films (figs. 10 and 11) is attributed to the presence of iron oxides and carbon, which evidently will themselves reduce the friction from that of clean steel.

SUMMARY OF RESULTS

The following results were obtained from an experimental investigation conducted to determine the oxidation characteristics of molybdenum disulfide MoS_2 and the effect of such oxidation on its role as a solid-film lubricant:

1. A coating of molybdenum disulfide MoS_2 serving as a high-temperature solid-film lubricant maintained low values of coefficient-of-friction during its oxidation as long as an effective subfilm of MoS_2 remained.
2. Films of the oxidation product of molybdenum disulfide MoS_2 , namely molybdenum trioxide MoO_3 , alone produced very high friction.
3. Molybdenum disulfide MoS_2 began to oxidize at a very low rate when heated in air at 750°F ; the rate increased steadily and became high at 1050°F and above.
4. Molybdenum disulfide MoS_2 maintained its original hexagonal structure when heated to 1000°F in vacuum.

Lewis Flight Propulsion Laboratory,
National Advisory Committee for Aeronautics,
Cleveland, Ohio, February 28, 1949.

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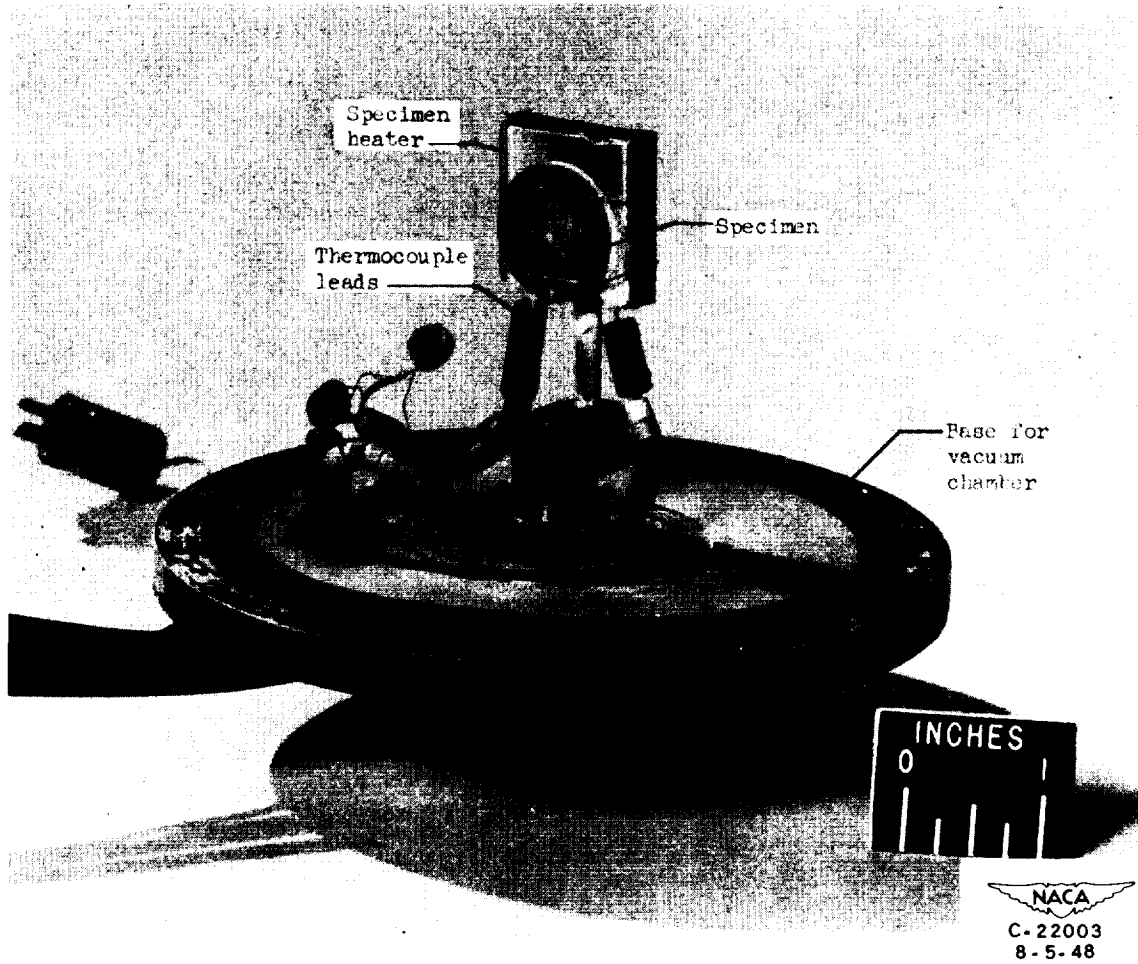


Figure 1. - Arrangement of specimen heater and specimen with embedded thermocouple for X-ray diffraction analysis of oxidation characteristics of molybdenum disulfide MoS_2 .

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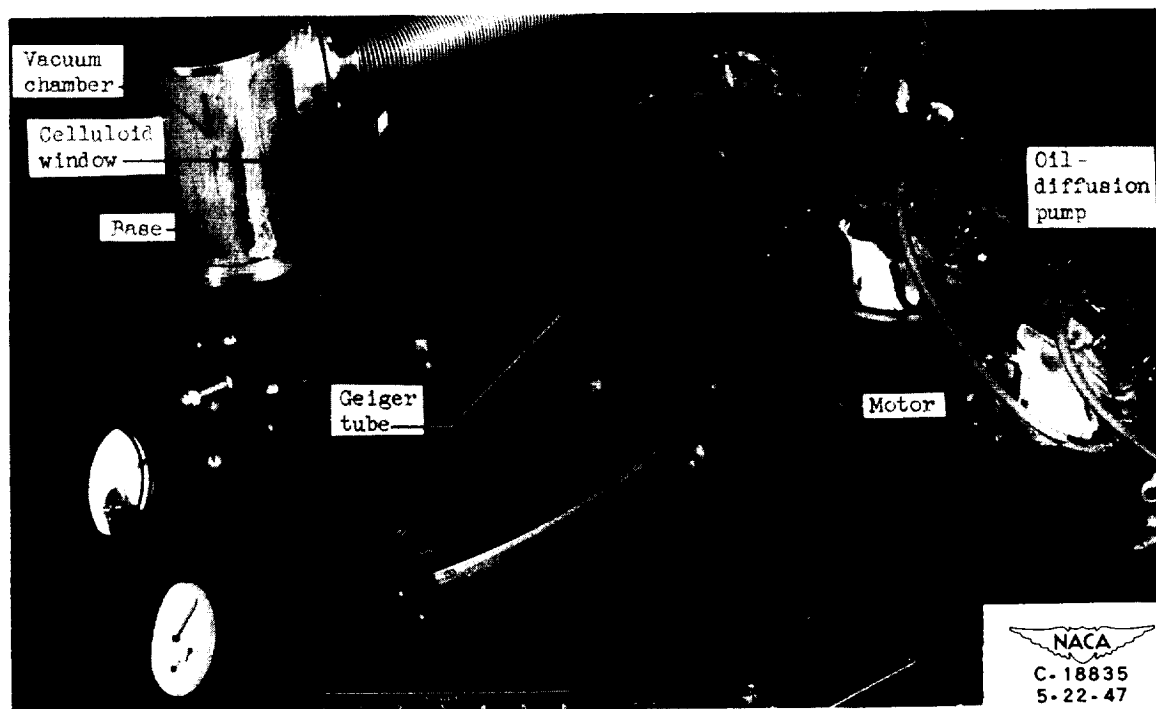


Figure 2. - X-ray spectrometer with vacuum chamber for determining by X-ray diffraction crystalline structure of molybdenum disulfide MoS_2 at high temperatures and low pressures.

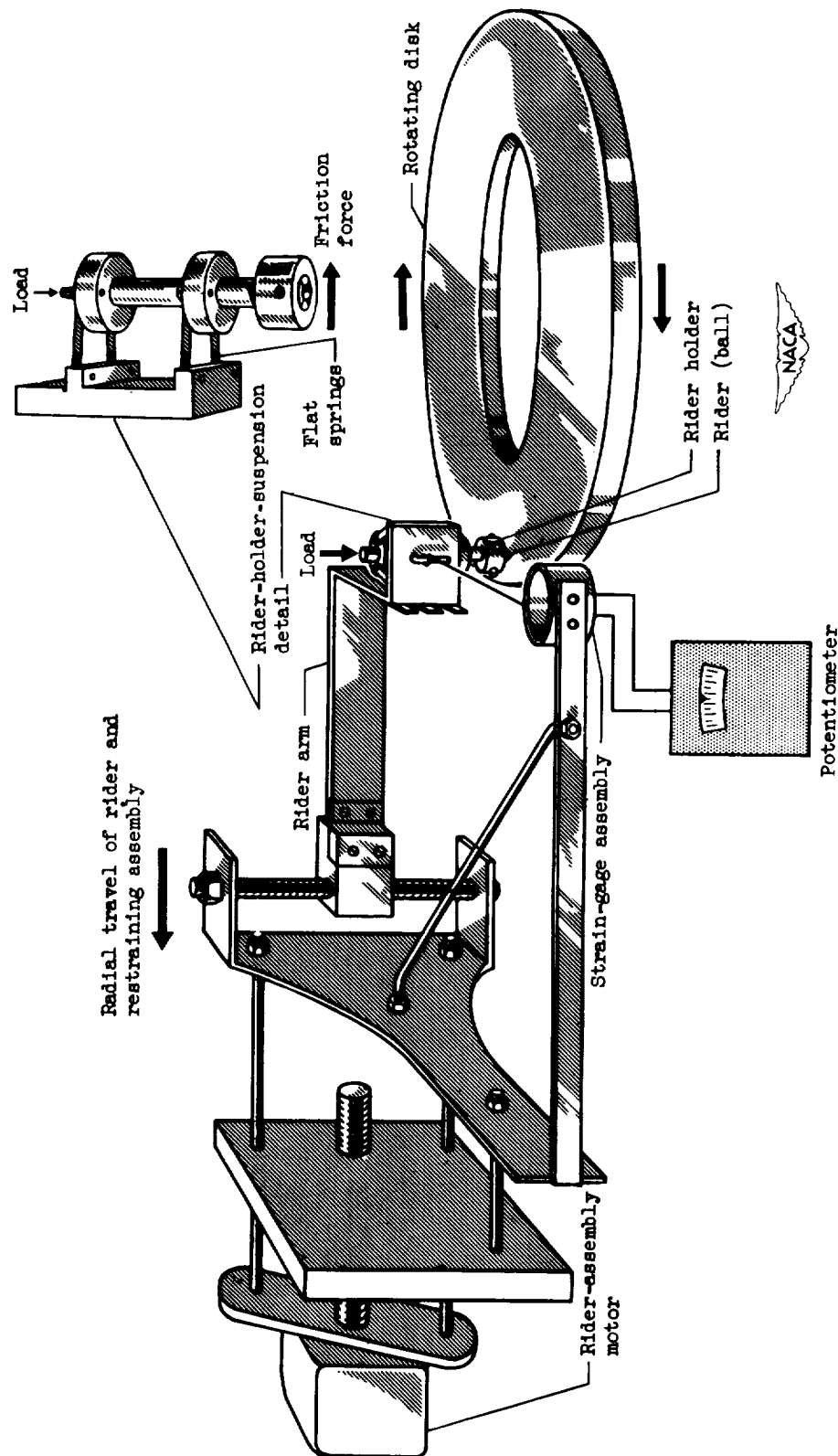
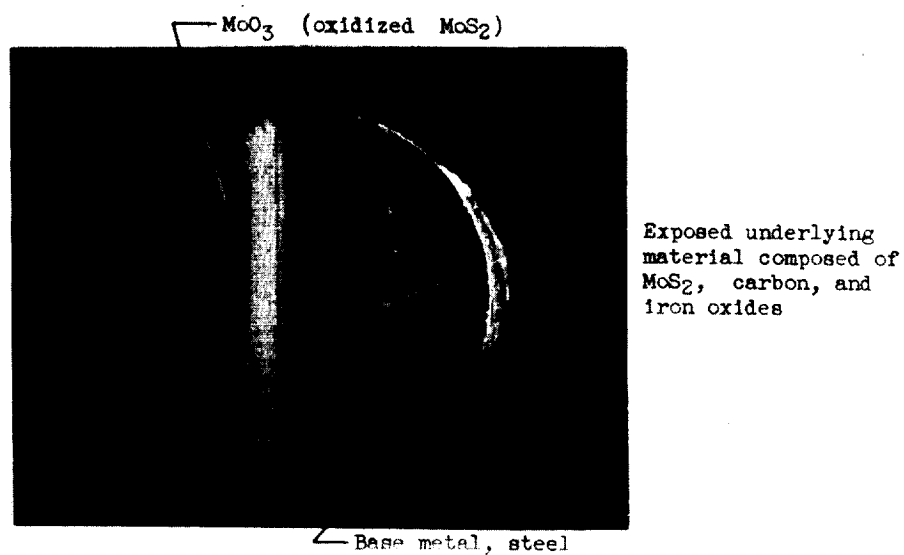


Figure 3. - Schematic diagram of sliding-friction apparatus.

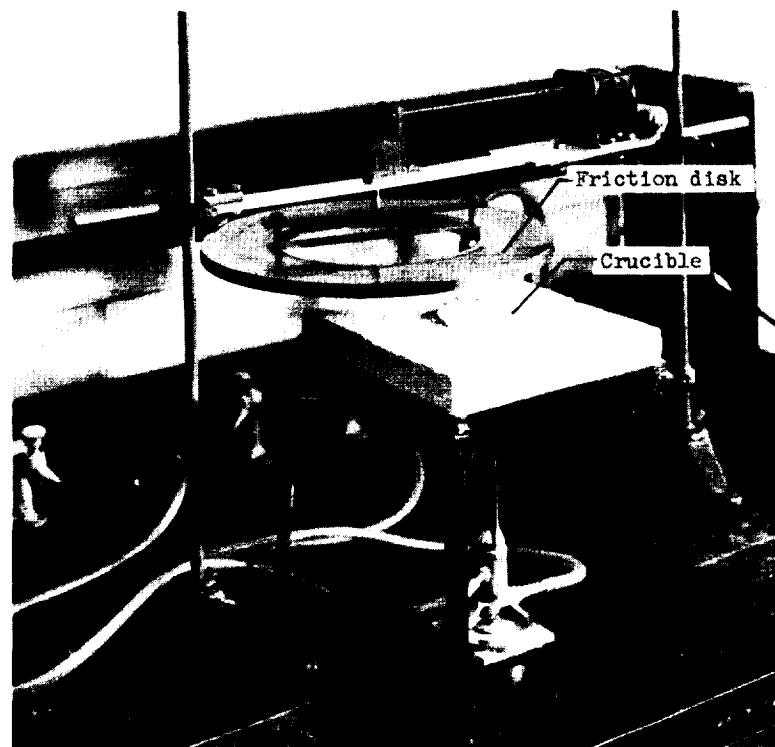
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Figure 4. - Molybdenum disulfide MoS₂ coated specimen that has been heated in air at 1000° F for 1/2 hour to partly oxidize molybdenum disulfide MoS₂ to molybdenum trioxide MoO₃. Identification made by electron diffraction.

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Figure 5. - Evaporation equipment for formation of uniform film of molybdenum trioxide MoO_3 on disk for friction experiments.

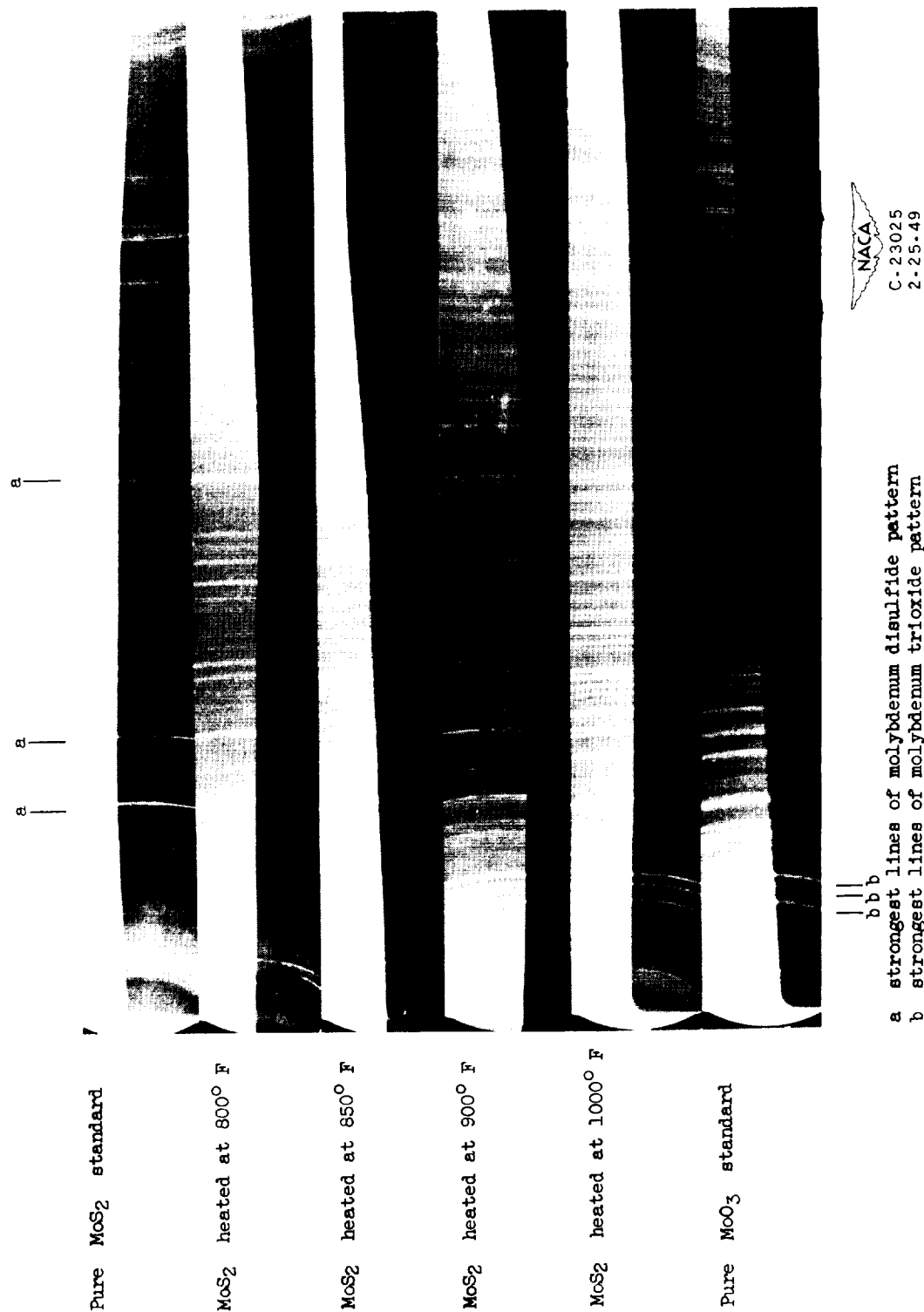


Figure 6. - X-ray diffraction patterns taken at room temperature, copper radiation, and nickel filter showing progress of oxidation of molybdenum disulfide MoS_2 to molybdenum trioxide MoO_3 when MoS_2 is heated in open crucible at indicated temperatures for 1/2 hour. The dark half of each pattern is the filtered portion.

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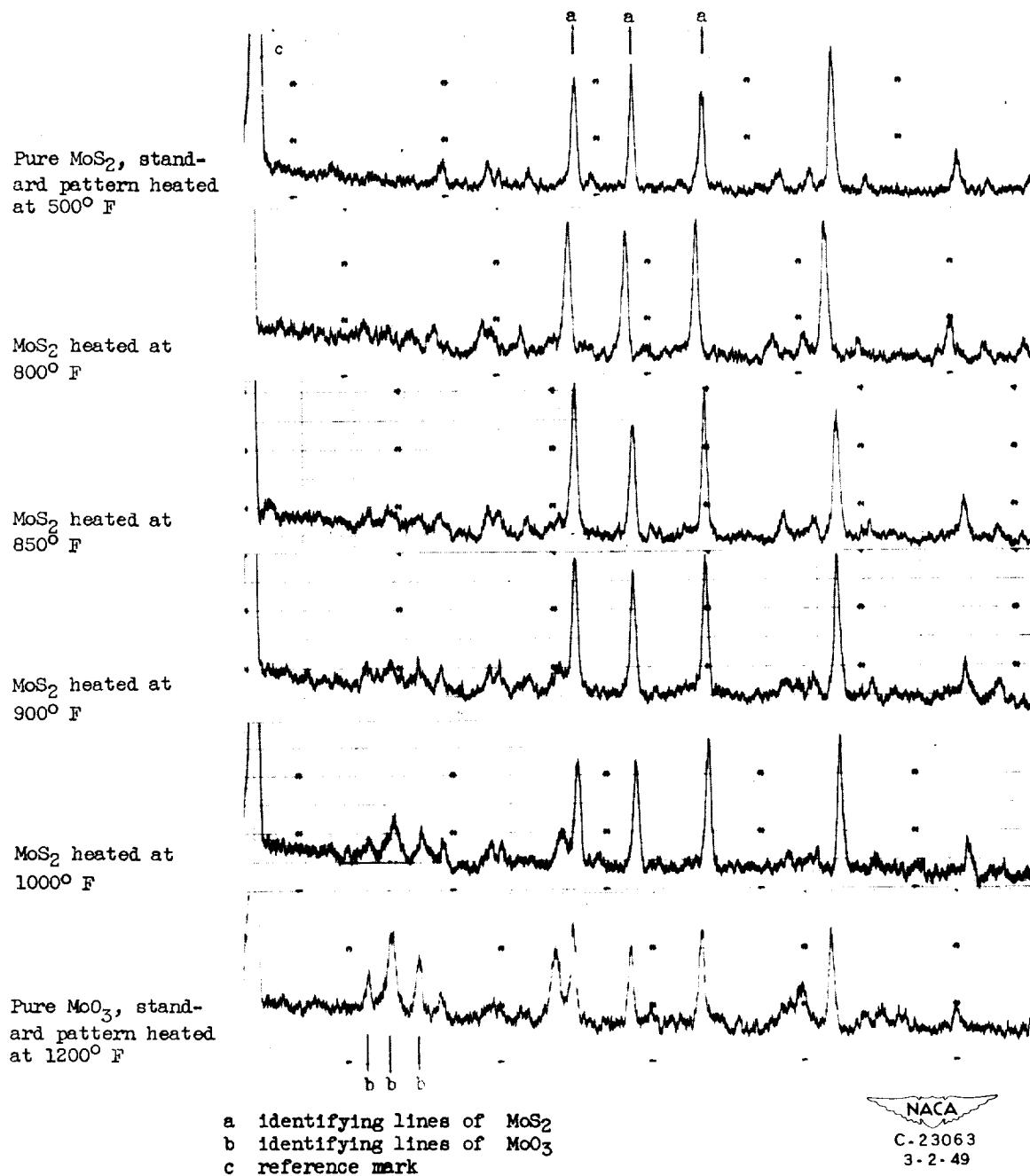


Figure 7. - Reproduction of tracings of X-ray diffraction patterns obtained from molybdenum disulfide MoS_2 heated in high-temperature X-ray diffraction camera for 3 hours at indicated temperatures. Appearance of identifying lines of molybdenum trioxide MoO_3 indicates degree of oxidation of MoS_2 .

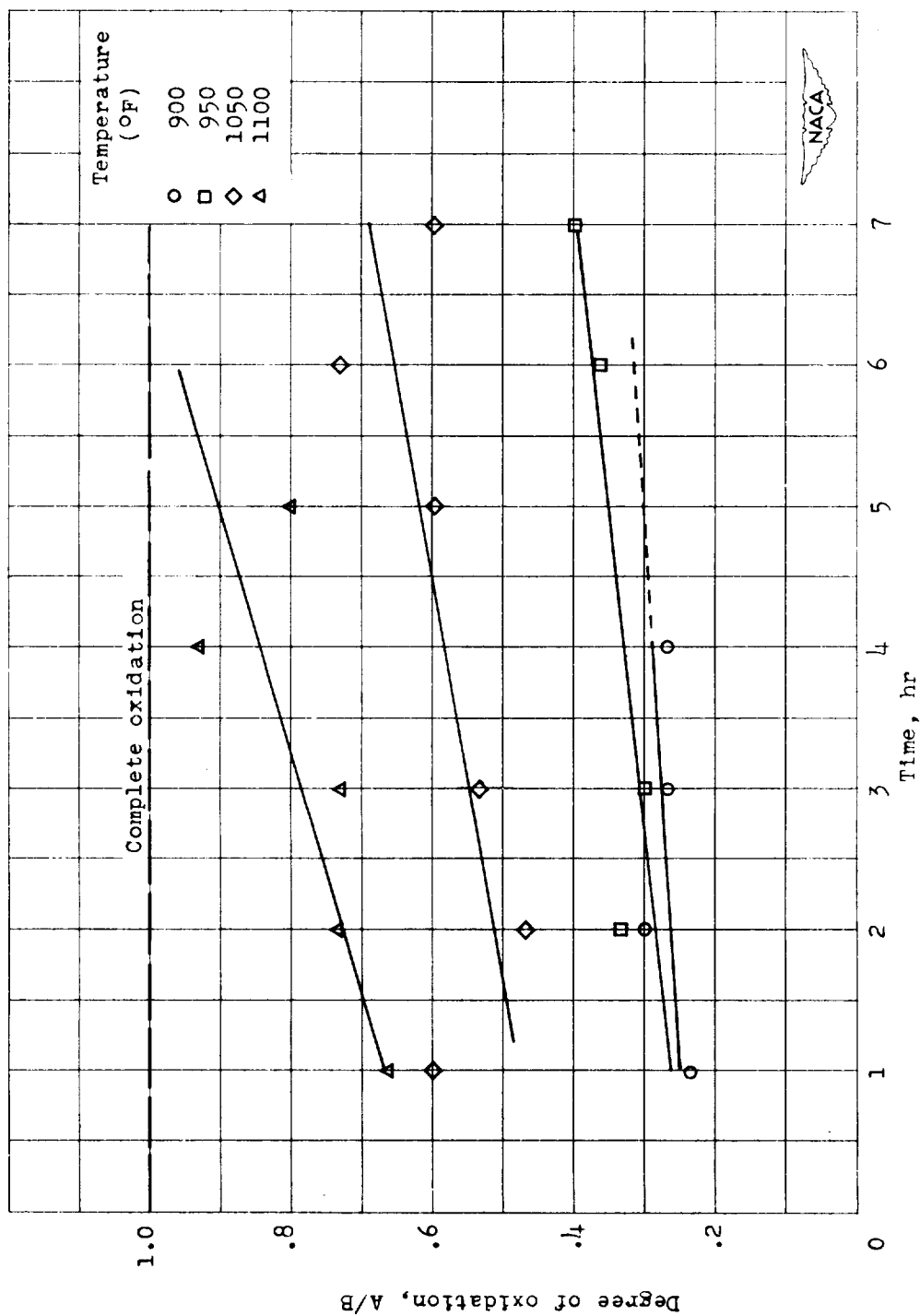


Figure 8. - Change in degree of oxidation (as expressed by ratio A/B) with time at various temperatures in oxidation of molybdenum disulfide MoS_2 . A, height of most intense line in tracing of X-ray diffraction pattern of molybdenum trioxide MoO_3 in partly oxidized specimen; B, height of most intense line in tracing of X-ray diffraction pattern of molybdenum trioxide MoO_3 in completely oxidized specimen.

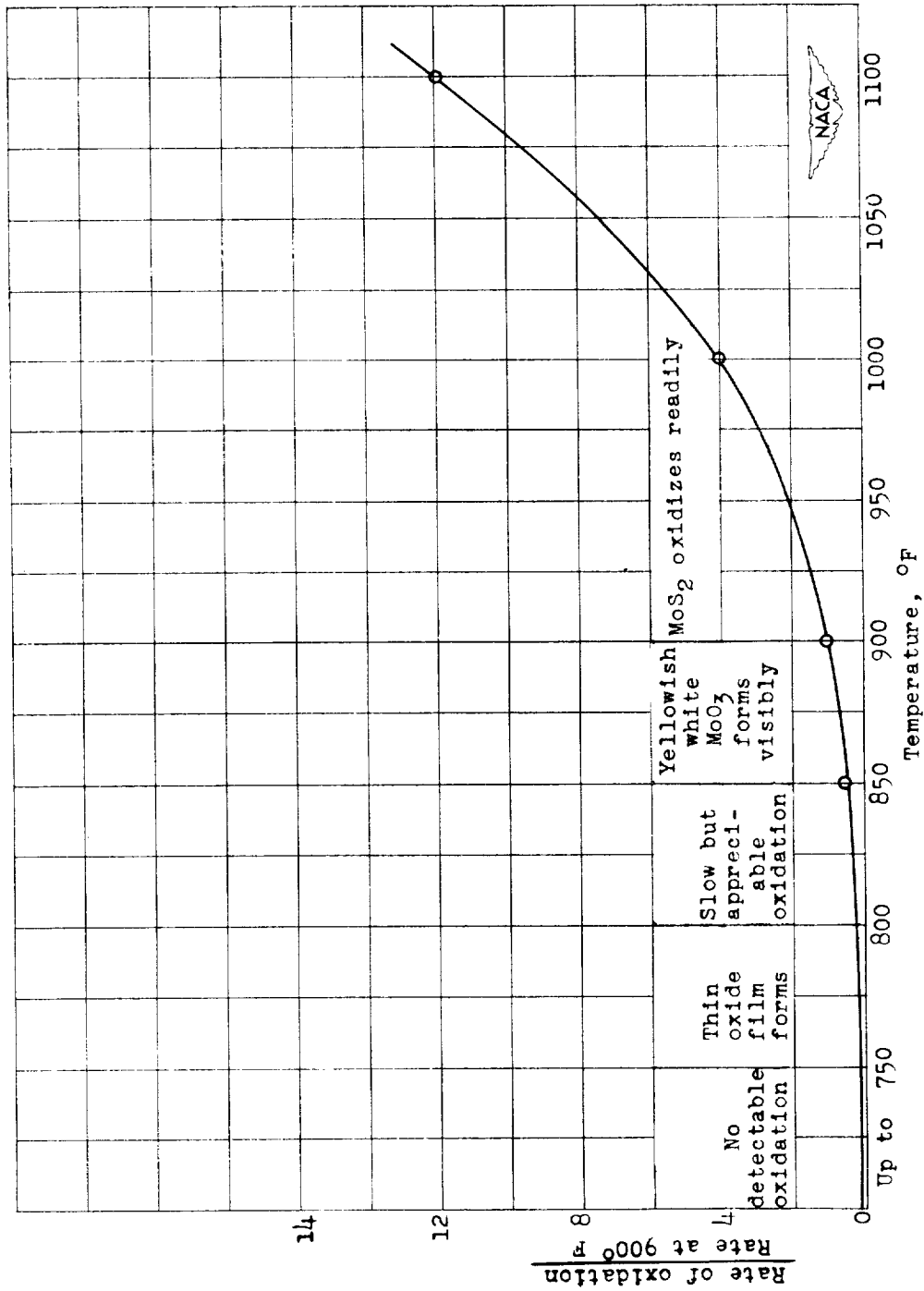


Figure 9. - Summarization of oxidation characteristics of molybdenum disulfide MoS_2 from room temperature to 1100° F, when exposed for 1/2 hour, expressed as ratio of rate of oxidation to rate at 900° F.

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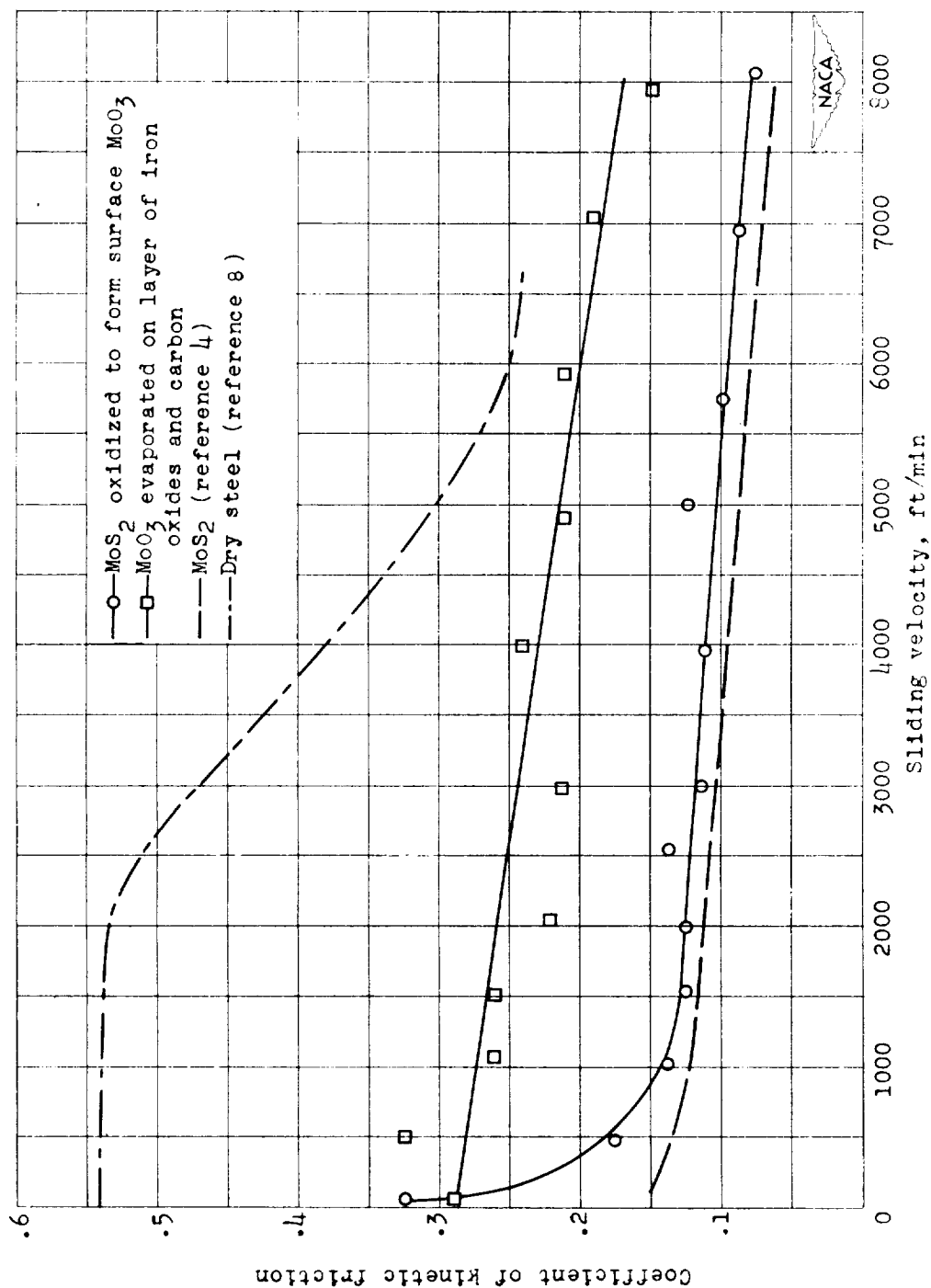


Figure 10. - Effect of sliding velocity on coefficient of friction for steel specimens coated with molybdenum disulfide MoS₂, partly oxidized molybdenum disulfide MoS₂, and molybdenum trioxide MoO₃. Load, 269 grams (126,000 lb/sq in. initial Hertz surface stress).

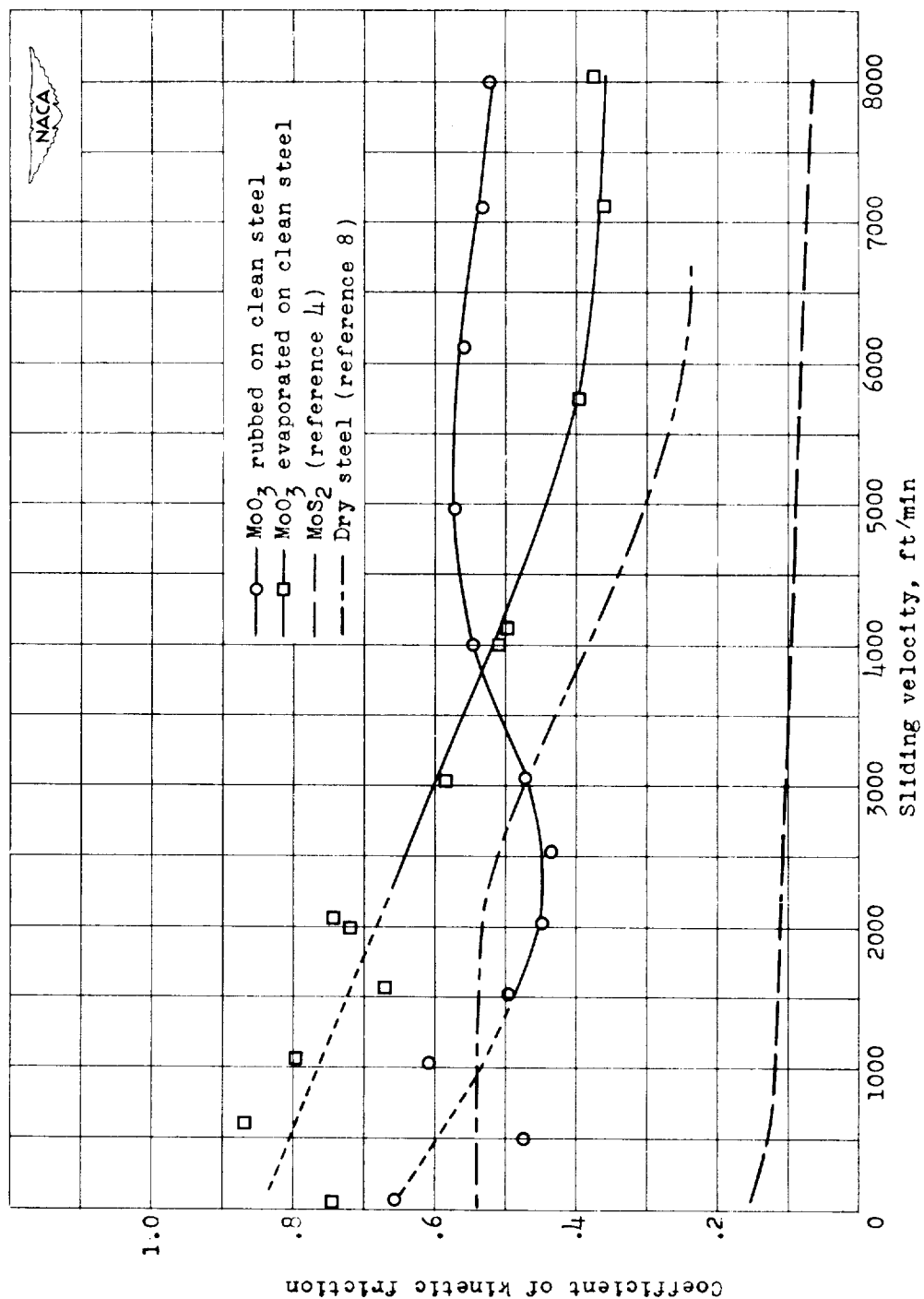


Figure 11. - Effect of sliding velocity on friction for steel specimens coated with molybdenum trioxide MoO₃. Load, 269 grams (126,000 lb/sq in. initial Hertz surface stress).